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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
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Process for conservation of a cellulosic material

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Process for conservation of a cellulosic material

The present invention concerns a process for conservation of a cellulosic material.

The process is useful notably for conservation of valuable documents on cellulosic support such as books, manuscripts or works of art, clothes, flags and the like.

During the past 150 years, archives and libraries have struggled to prevent the aging of paper, i.e. notably yellowing and embrittlement of paper in documents and books. Many treatments to avoid or stop this aging have been proposed. The primary goals of this treatment are either to transform the paper into another, more stable medium or stabilise the paper against degradation processes.

Above documents are subject to deterioration notably because of the acid content in most of the cellulosic materials. Another serious problem encountered in the conservation of books and documents made of paper stems from the readily oxidizable nature of the material. Oxidation not only results in the discoloration of paper but also a considerable mechanical weakening of the text's support. Such discoloration is favoured by light radiation, which constitutes other significant source of degradation in paper. The auto-oxidizing mechanism of degradation which occurs in cellulose during the ageing process (in atmospheric oxygen) is also important in library conservation.

Canadian patent application CA-A-2142195 describes paper deacidification compositions containing methoxymagnesium methylcarbonate or ethoxymagnesium ethylcarbonate in a solvent diluted with a hydrochlorofluorocarbon or a hydrofluorocarbon.

This and other known conservation techniques are not entirely satisfactory as they may cause harm to inks and colours, thus giving rise to problems like ink or colour bleeding, formation of Newton rings and/or white deposits.

It was desirable to find a conservation process, notably a deacidification process which is effective and does not display the problems above, or which at least allows to minimise said problems.

The invention concerns in consequence a process for conservation of a cellulosic material, comprising a treatment wherein said cellulosic material is

contacted with a stabilising agent, and at least one of the cellulosic material or the stabilising agent is cooled before and/or during the treatment.

The cellulosic material is generally a printed and/or coloured cellulosic material.

The process according to the invention is compatible with the presence of other materials such as in particular leather used e.g. in book covers.

In the process according to the invention, at least one of the cellulosic material or the stabilising agent is generally cooled to a temperature which is less than 20°C. Often this temperature is equal to or less than 10°C. More often, this temperature is equal to or less than 0°C. Preferably, this temperature is equal to or less than -10°C. A temperature of about -15°C is particularly preferred.

In the process according to the invention, at least one of the cellulosic material or the stabilising agent is generally cooled to a temperature which is equal to or higher than -50°C. Often, this temperature is equal to or higher than -30°C. Preferably, the temperature is equal to or higher than -20°C.

In a first preferred embodiment, at least the cellulosic material is cooled.

In a second embodiment, only the stabilising agent is cooled. If the stabilising agent is a composition of several constituents, one or more of the constituents can eventually be cooled before forming the composition.

In a third, preferred, embodiment the treatment is carried out at the abovementioned temperature. That means that the system consisting of cellulosic material and stabilising agent is brought to these temperatures. Generally, in this case, the system is kept at that temperature for a time sufficient to ensure the stabilising effect.

It is advantageous, in particular in the third embodiment, to ensure that the cellulosic material and the stabilising agent have substantially the same temperature as they are being contacted. Good results have been achieved with a temperature difference between the cellulosic material and the stabilising agent of less than 20°C. Preferably, this temperature difference is less than 10°C and more preferably, it is less than 5°C. Most preferably, the temperature difference is about 1°C or less.

The process according to the invention is often carried out at a pressure at which the stabilising agent is in the liquid phase, being understood that suspensions, dispersions and slurries are also considered as liquid phases. A solution is preferred when the stabilising agent is in the liquid phase.

Alternatively, the process according to the invention can be carried out with a stabilising agent which is in the vapour phase under the treatment conditions.

Typical working pressures in the process according to the invention range from 1 to 10 bar.

In the process according to the invention, the duration of the treatment is generally at most 50 hours, preferably at most 10 hours. The duration of the treatment is more preferably less than or equal to about 3 hours. A duration of the treatment equal to our less than 1 hour, for example 30-45 min is more particularly preferred.

It has been found, surprisingly, that the process according to the invention allows for short treatment times in spite of cooling stabilising agent and/or cellulosic material.

In a particular embodiment of the process according to the invention, the cellulosic material is not dried before the treatment.

In another particular embodiment of the process according to the invention, the cellulosic material is slightly dried before the treatment so that it looses about 1 – 2% of moisture content by weight relative to the total weight of the cellulosic material before treatment. Such slight drying can be brought about by gentle heating of the cellulosic material to 30 to 50°C, preferably about 40°C.

A first particular way of carrying out the process according to the invention comprises :

(a) cooling the stabilising agent;
(b) contacting the cellulosic material and the stabilising agent cooled in step (a), preferably in a treatment chamber which has optionally been cooled before introducing the cellulosic material;
(c) optionally, separating excess quantities of stabilising agent or constituents of the stabilising agent from the cellulosic material;
(d) optionally, recovering excess quantities or constituents separated in step (c).

A second particular way of carrying out the process according to the invention comprises :

(a) providing a treatment chamber equipped with a cooling device, which treatment chamber is cooled down before the treatment;
(b) introducing cooled cellulosic material into the treatment chamber;
(c) supplying the optionally cooled stabilising agent to said treatment chamber so as to contact the stabilising agent with the cellulosic material;

(d) optionally, separating excess quantities of stabilising agent or constituents of the stabilising agent from the cellulosic material;

(e) optionally, recovering excess quantities or constituents separated in step (d).

In the process according to the invention, the stabilising agent is often selected from fibre strengtheners, sizing agents, antioxidants, biocides and/or deacidification reagents.

Among fibre strengtheners and sizing agents, cellulose derivatives and/or natural or non-natural polymers can suitably used. Specific examples of cellulose derivatives are selected from carboxymethylcellulose, methylcellulose, ethylcellulose and cellulose ethers. Specific examples of non-natural polymers are selected from styrene/acrylate copolymers, polyurethanes and polyamides. A specific natural polymer is starch.

Among antioxidants, derivatives of oxidizable arylcarboxylic acids, in particular hydroxyarylcarboxylic acids can suitably be used. Esters of arylcarboxylic acids are preferred. In this case the ester is generally an alkyl ester, preferably an alkyl ester derived from a linear, branched or cyclic alkyl radical having generally from 1 to 10, preferably from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl, isopropyl or butyl radicals, or their mixtures.

In a particularly preferred embodiment a derivative, in particular an alkyl ester of the p-hydroxibenzoic acid is used which is preferably selected among methyl p-hydroxibenzoate, ethyl p-hydroxibenzoate, propyl p-hydroxibenzoate, butyl p-hydroxibenzoate and their blends.

Preferred biocides correspond to the antioxidants described herebefore.

In the process according to the invention, the stabilising agent is preferably a deacidification agent

In this case, the deacidification agent generally comprises a base which can be selected for example from basic metal derivatives, from organometallic derivatives or from alkaline monomers such as acrylates.

Examples of particular basic metal derivatives suitable for use in the present invention include the oxides, hydroxides, carbonates and bicarbonates of zinc and metals in Group I, II and IV of the Periodic Table. According to certain embodiments, the bases are preferably oxides, hydroxides, carbonates and bicarbonates of magnesium, titanium, calcium, sodium, potassium, zinc, or combinations of two or more thereof. Examples of agents include magnesium carbonate, magnesium bicarbonate, magnesium oxide, magnesium methyl carbonate, titanium alcoholates, calcium oxide, sodium hydroxide, potassium

hydroxide, calcium hydroxide, zinc carbonate, zinc bicarbonate, zinc oxide, and combinations of two or more thereof.

Basic alkaline earth metal derivatives in particular magnesium compounds or salts are preferred. Most preferred bases are selected from magnesium alkoxycarbonates such as carbonates derived from magnesiumdimethanolate, magnesiumdiethanolate and in particular magnesiumdipropanolate.

The deacidification agent may optionally comprise a solvent selected for example from alcohols, in particular having 1 to 4 carbon atoms, and non-halogenated or halogenated hydrocarbon solvents or ethers. Such solvents include for example methanol, ethanol, isopropanol, n-propanol, isobutanol, propane, butanes, pentanes, isohexanes, heptanes, alkylsiloxanes, HFE-7100 and HFE-7200. n-propanol is preferred

In another embodiment, the solvent comprises a fluorinated alcohol such as 2,2,3,3,3-pentafluoro-1-propanol.

In a preferred embodiment of the invention, the stabilising agent, in particular the deacidification agent comprises a hydrofluoroalkane. Suitable hydrofluoroalkanes generally comprise from 1 to 10, preferably from 2 to 6 carbon atoms.

Specific hydrofluoroalkanes are selected from difluoromethane (HFC-32), 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,3,3-pentafluorobutane (HFC-365mfc) and 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee). HFC-227ea, HFC-134a and their mixtures are preferred.

A surfactant may optionally be present, in particular if no solvent is used.

The moisture content of optional solvent and hydrofluoroalkane is generally less than 1000 mg/kg. This content can also be below 200 or 100 mg/kg.

In a most preferred embodiment, the deacidification agent is a composition of magnesium propylcarbonate, propanol, in particular n-propanol, and HFC-227ea and/or HFC-134a. This composition and its manufacture is described in EP-1111128 whose content is incorporated by reference in the present application. This particular deacidification agent is generally in the form of a solution and is comprised of carbonated magnesium di-n-propylate preferably in n-propanol, and an HFC diluent selected from 1,1,1,2-tetrafluoroethane (HFC-

134a) and 1,1,1,2,3,3,3-heptafluoropropane (HFC-227). Carbonated magnesium di-n-propylate is a solid with the formula (CH3CH2CH2O)2 MgOCO. The concentration of carbonated magnesium di-n-propylate in n-propanol is preferably between 30 and 70% (weight by weight relative to the total weight of carbonated magnesium di-n-propylate and n-propanol). A composition comprising 1.5 – 2.0% (weight by weight relative to the total weight of the composition) of carbonated magnesium di-n-propylate, 3.0 - 4.0% of n-propanol and the remainder consisting essentially of HFC is more particularly preferred.

CLAIMS

1 – Process for conservation of a cellulosic material, comprising a treatment wherein said cellulosic material is contacted with a stabilising agent, and at least one of the cellulosic material or the stabilising agent is cooled before and/or during the treatment.

2 – Process according to claim 1, wherein at least one of the cellulosic material or the stabilising agent is cooled to a temperature which is less than 20°C.

3 – Process according to claim 2, wherein the temperature is from -50°C to 0°C, preferably from -20°C to -5°C.

4 – Process according to claim 2 or 3, wherein the treatment is carried out at said temperature.

5 – Process according to anyone of claims 1 to 4, wherein the cellulosic material and the stabilising agent have substantially the same temperature as they are being contacted.

6 – Process according to anyone of claims 1 to 4, wherein the stabilising agent is selected from fibre strengtheners, sizing agents, antioxidants, biocides and/or deacidification agents.

7 – Process according claims 6, wherein the stabilising agent is a deacidification agent.

8 – Process according to claim 7, wherein the deacidification agent comprises a base selected from basic alkaline earth metal derivatives, in particular magnesium or calcium compounds or salts.

9 – Process according to claim 7 or 8, wherein the deacidification agent comprises a solvent selected from alcohols, in particular having 1 to 4 carbon atoms, and non-halogenated or halogenated hydrocarbon solvents or ethers.

10 – Process according to anyone of claims 7 to 9, wherein the deacidification agent comprises a hydrofluoroalkane, preferably selected from HFC-227ea and HFC-134a.

11 – Process according to claim 10, wherein the deacidification agent is a composition of magnesium propylcarbonate, propanol and HFC-227ea.

12 – Process according to anyone of claims 1 to 11, wherein the treatment is carried out for a duration of from 1 to 50 hours.

13 – Process according to anyone of claims 1 to 12, wherein the cellulosic material is not dried before the treatment.

14 – Process according to anyone of claims 1 to 12, wherein the cellulosic material is dried before the treatment so that it looses about 1% or 2% of moisture content weight by weight.

15 – Process according to anyone of claims 1 to 14, which comprises :

(a) cooling the stabilising agent;

(b) contacting the cellulosic material and the stabilising agent cooled in step (a), preferably in a treatment chamber which has optionally been cooled before introducing the cellulosic material;

(c) optionally, separating excess quantities of stabilising agent or constituents of the stabilising agent from the cellulosic material;

(d) optionally, recovering excess quantities or constituents separated in step (c).

16 – Process according to anyone of claims 1 to 14, which comprises

(a) providing a treatment chamber equipped with a cooling device, which treatment chamber is cooled before the treatment;

(b) introducing cooled cellulosic material into the treatment chamber;

(c) supplying the optionally cooled stabilising agent to said treatment chamber so as to contact the stabilising agent with the cellulosic material;

(d) optionally, separating excess quantities of stabilising agent or constituents of the stabilising agent from the cellulosic material;

(e) optionally, recovering excess quantities or constituents separated in step (d).

ABSTRACT

Process for conservation of a cellulosic material

Process for conservation of a cellulosic material, comprising a treatment wherein said cellulosic material is contacted with a stabilising agent, and at least one of the cellulosic material or the stabilising agent is cooled before and/or during the treatment. A deacidification agent comprising magnesiumdipropoxycarbonate, propanol and an HFC selected from HFC-134a and HFC-227ea is particularly preferred as stabilising agent.

No figure.